جامعة الانبار

كلية **: الصيدلة**

قسم : **الكيمياء الصيدلانية**

اسم المادة باللغة العربية**: الكيمياء التحليلية**

اسم المادة باللغة الإنكليزية: **Analytical Chemistry**

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عنوان المحاضرة باللغة العربية: مراجعة المفاهيم الاساسية

عنوان المحاضرة باللغة الإنكليزية: **Review of Elementary of Concepts**

**** Salts***

Salts are formed by the reactions of cations and anions. Some of the salts are anhydrous like NaCl, KCl, $KMnO_4$ and $K_2Cr_2O_7$. Other salts are hydrous such as $CaCl_2.2H_2O$, $CuSO_4.5H_2O$ and $ZnSO_4.7H_2O$. Salts exist in its solid state as ions, therefore, sodium chloride is ionized in its crystalline case into Na^+ which is surrounded by six ions of Cl^-, and each Cl^- is surrounded by six ions of Na^+. These ions are attached to each other by electrostatic strengths. Thus, these salts are completely ionized in solvents of dielectric constant like water.

1.6 Chemical Units of Weight

In the laboratory, the mass of a substance is ordinarily determined in such metric units as the kilogram (kg), the gram (g), the milligram (mg), the microgram (µg), the nanogram (ng), or the picogram (pg).

$$g = 10^3 \text{ mg} = 10^6 \text{ µg} = 10^9 \text{ ng} = 10^{12} \text{ pg} = 10^{-3} \text{ kg}$$

For chemical calculations, however, it is more convenient to employ mass units that express the weight relationship or stoichiometry among reacting species in terms of small whole numbers. The gram formula weight, the gram molecular weight, and the gram equivalent weight are employed in analytical work for this reason. These terms are often shortened to the formula weight, the molecular weight and the equivalent weight.

One molecular weight of a species contains 6.02×10^{23} particles of that species; this quantity is frequently referred to as the ***mole***. In a similar way, the formula weight represents 6.02×10^{23} units of the substance, whether real or not, represented by the chemical formula.

Example 1

A 25.0 g sample of H_2 contains:

$$\frac{25.0\ g}{2.016\ g/mole} = 12.4 \text{ moles of } H_2$$

$$12.4 \text{ moles} \times \frac{6.02\times10^{23} \text{ molecules}}{\text{Mole}} = 7.47\times10^{24} \text{ molecules } H_2$$

The same weight of NaCl contains:

$$\frac{25.0\ g}{58.44\ g/fw} = 0.428 \text{ fw NaCl}$$

which corresponds to 0.428 mole Na^+ and 0.428 mole Cl^-

1.7 Equivalent Weight

It is the mass of a given substance which will combine with or displace a fixed quantity of another substance.

For acids:

It is the weight of acid that contains one equivalent of a proton.

$$\text{equivalent weight} = \frac{\text{molar mass}}{\text{no. of equivalent hydrogen ions}}$$

Example 2

Calculate the equivalent weights for the following acids: HCl, H_2SO_4, H_3PO_4. Atomic weights for H = 1, O = 16, Cl = 35.5, S = 32, P = 31.

$$\text{equivalent weight for HCl} = \frac{\text{molar mass}}{\text{no. of equivalent hydrogen ions}}$$

$$= \frac{1 + 35.5}{1} = 36.5 \text{ gram/equivalent}$$

$$\text{for } H_2SO_4 = \frac{(2\times1) + 32 + (16\times4)}{2} = 49$$

$$\text{for } H_3PO_4 = \frac{(3\times1) + 31 + (16\times4)}{3} = 32.67$$

For bases:

It is the weight of base that contains one equivalent of an hydroxide.

$$\text{equivalent weight} = \frac{\text{molar mass}}{\text{no. of equivalent hydroxide ions}}$$

Example 3

Calculate the equivalent weights for the following bases: NaOH, $Ca(OH)_2$, $Al(OH)_3$. Atomic weights for H = 1, O = 16, Na = 23, Ca = 40, Al = 26.98.

$$\text{equivalent weight for NaOH} = \frac{\text{molar mass}}{\text{no. of equivalent hydroxide ions}}$$

$$= \frac{23 + 16 + 1}{1} = 40$$

gram/equivalent

$$\text{for } Ca(OH)_2 = \frac{40 + [(16 + 1)]2}{2} = 37$$

$$\text{for } Al(OH)_3 = \frac{26.98 + [(16 + 1)]3}{3} = 25.99$$

For salts:

It is the weight of the salt that contains the equivalent weight of one of its ions.

$$\text{equivalent weight for salt} = \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}}$$

$$= \frac{\text{molar mass}}{\text{no. of acidic radical ions} \times \text{oxidation no.}}$$

Example 4

Calculate the equivalent weights for the following salts: Na_2O, Na_2CO_3, $Al_2(SO_4)_3$. Atomic weights for O = 16, C = 12, Na = 23, S = 32, Al = 26.98.

$$\text{equivalent weight for } Na_2O = \frac{\text{molar mass}}{\text{no. of metal ions} \times \text{oxidation no.}}$$

$$= \frac{(23 \times 2) + 16}{2 \times 1} = 31$$ gram/equivalent

$$\text{for } Na_2CO_3 = \frac{(23 \times 2) + 12 + (16 \times 3)}{2 \times 1} = 53$$

$$\text{for } Al_2(SO_4)_3 = \frac{(26.98 \times 2) + [32 + (16 \times 4)]\,3}{2 \times 3} = 56.99$$

For salts in precipitation reactions:

The equivalent weight of salts in precipitation reactions is the weight of substance in gram that precipitates quantity equivalent to quantity of 1 gram of hydrogen, or the equivalent weight of another substance in the same reaction.

$$\text{equivalent weight for salt} = \frac{\text{molar mass}}{\text{sum of oxidation numbers of the part participates in precipitate formation}}$$

Example 5

Calculate the equivalent weight for the substances participate in the reaction of AgCl precipitation. Atomic weights for Ag = 108, N = 14, O = 16, Na = 23, Cl = 35.5.

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

$$\text{equivalent weight for } AgNO_3 = \frac{\text{molar mass for } AgNO_3}{\text{oxidation number of Ag}}$$

$$= \frac{108 + 14 + (16 \times 3)}{1} = 170 \text{ gram/equivalent}$$

$$\text{equivalent weight for NaCl} = \frac{\text{molar mass for NaCl}}{\text{oxidation number of } Cl^-}$$

$$= \frac{35.5 + 23}{1} = 58.5$$

For oxidation-reduction agents:

The oxidation-reduction reactions involve transfer of electrons from one substance to another.

$$\text{equivalent weight for oxidation or reduction agent} = \frac{\text{molar mass}}{\text{the difference between oxidation numbers}}$$

Example 6

Calculate the equivalent weight for $FeSO_4$ and $KMnO_4$ in the following reaction, which permanganate solution oxidizes iron sulphate. Atomic weights for Fe = 56, S = 32, O = 16, K = 39, Mn = 55.

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The ferrous oxidized to ferric:

$$Fe^{2+} \longrightarrow Fe^{3+} + e^- \quad \text{(oxidation)}$$

the difference between oxidation numbers = +3 – (+2) = +1

$$\text{equivalent weight for } FeSO_4 = \frac{\text{molar mass for } FeSO_4}{1}$$

$$= \frac{152}{1} = 152 \text{ gram/equivalent}$$

the manganese gain 5 electrons:

$$Mn^{7+} + 5e^- \longrightarrow Mn^{2+} \quad \text{(reduction)}$$

the difference between oxidation numbers = +7 – (+2) = 5

$$\text{equivalent weight for } KMnO_4 = \frac{\text{molar mass for } KMnO_4}{5}$$

$$= \frac{158}{5} = 31.6$$

1.8 Methods of Expressing Solutions Concentration

1- *Mass percentage w/w%* $= \frac{\text{g solute}}{\text{g solution}} \times 100$

5% solution of NaCl means that 5 g of NaCl dissolved in 95 g water.

Example 7

Calculate the mass percentage of 200 g solution contains 25 g sodium sulphate.

$$\text{mass percentage w/w\%} = \frac{\text{g solute}}{\text{g solution}} \times 100$$

$$= \frac{25}{200} \times 100 = 12.5\%$$

Example 8

Calculate the mass percentage for a solution prepared by dissolving 15 g of $AgNO_3$ in 100 cm^3 water. The density of water is 1 g/cm^3.

$$\text{weight of solvent} = \text{volume} \times \text{density}$$

$$= 100\ cm^3 \times 1\ g/cm^3$$

$$= 100\ g$$

$$\text{weight of solution} = 100 \text{ g solvent} + 15 \text{ g solute}$$
$$= 115 \text{ g}$$

$$\text{mass percentage w/w\%} = \frac{\text{g solute}}{\text{g solution}} \times 100$$

$$= \frac{15}{115} \times 100$$

$$= 13.04\%$$

2- *Volume percentage v/v%* $= \dfrac{\text{ml solute}}{\text{ml solution}} \times 100$

10% solution of alcohol means that 10 ml alcohol is added to enough solvent in order to reach 100 ml volume (addition of 90 ml solvent).

Example 9

10 g of organic solvent (density 1.5 g/cm^3) was added to 90 g water, the density of the solution become 1.1 g/cm^3. Calculate the v/v% and the w/w% concentrations of the organic substance in the solution.

$$\text{weight of solution} = 90 \text{ g} + 10 \text{ g} = 100 \text{ g}$$

$$\text{mass percentage w/w\%} = \frac{10 \text{ g}}{100 \text{ g}} \times 100$$

$$= 10\%$$

$$\text{volume of solution} = \frac{\text{weight}}{\text{density}} = \frac{100}{1.1} = 90.90 \text{ ml}$$

$$\text{volume of solute} = \frac{\text{weight}}{\text{density}} = \frac{10}{1.5} = 6.67\ \text{ml}$$

$$\text{volume percentage v/v\%} = \frac{6.67\ \text{ml}}{90.90\ \text{ml}} \times 100 = 7.3\%$$

3- *Mass/volume percentage w/v%* $= \dfrac{\text{g solute}}{\text{ml solution}} \times 100$

Example 10

Calculate the weight of sodium chloride salt in 500 ml solution of a 0.85 %w/v concentration.

$$\text{w/v\%} = \frac{\text{g solute}}{\text{ml solution}} \times 100$$

$$0.85 = \frac{\text{g}}{500} \times 100 = 4.25\ \text{g}$$

4- *Parts per million (ppm)* $= \dfrac{\text{mg solute}}{\text{kg solvent}}$

and there are:

$$\text{Parts per thousand (ppt)} = \frac{\text{g solute}}{\text{kg solvent}}$$

$$\text{Parts per billion (ppb)} = \frac{\mu\text{g solute}}{\text{kg solvent}}$$

Example 11

A weight of a sample 345 g contains 3 mg Hg, what is the concentration of Hg in the sample in ppm?

$$\text{parts per million (ppm)} = \frac{\text{mg solute}}{\text{kg solvent}}$$

$$\text{(ppm)} = \frac{3}{0.345} = 7.35 \text{ ppm}$$

Example 12

A sample contains 4.8 parts per billion arsine, if the weight of the sample is 525 g, how many µg arsine present in the sample?

$$\text{parts per billion (ppb)} = \frac{\mu\text{g solute}}{\text{kg solvent}}$$

$$4.8 = \frac{\mu\text{g arsine}}{0.525}$$

$$\mu\text{g arsine} = 2.52$$

5- *Molar concentration (M)*

It is the number of molar weights of the solute in 1 liter of solvent.

$$\text{Molarity (M)} = \frac{\text{no. of molar weights of solute}}{\text{volume of solution in liter}}$$

$$\text{no. of molar weights} = \frac{\text{weight of substance in g}}{\text{molar mass}}$$

$$\text{Molar concentration (M)} = \frac{\dfrac{\text{weight of substance in g}}{\text{molar mass}}}{\dfrac{\text{volume of solution in ml}}{1000}}$$

$$= \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$\text{weight of substance} = M \times \text{molecular weight} \times \frac{\text{volume ml}}{1000}$$

Example 13

Calculate the molar concentration (M) of a solution prepared by dissolving 29.35 g of NaCl in 200 ml water. Atomic weights for Na = 22.99, Cl = 35.45.

$$M = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$= \frac{29.35 \times 1000}{200 \times 58.44} = 2.5 \text{ molar}$$

Example 14

Calculate the weight of $AgNO_3$ needed to prepare 500 ml solution of a concentration 0.1250 M. Molecular weight of $AgNO_3$ is 169.9.

$$M = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{volume of solution in ml}}$$

$$\text{weight of } AgNO_3 = M \times \text{molecular weight} \times \frac{\text{volume ml}}{1000}$$

$$\text{weight of } AgNO_3 = 0.125 \times 169.9 \times \frac{500}{1000}$$

$$= 10.62 \text{ g}$$

6- *Normal concentration (N)*

It is the number of equivalent weights of the solute dissolved in liter of the solvent.

$$\text{Normality (N)} = \frac{\text{no. of equivalent weights of solute}}{\text{volume of solution in liter}}$$

$$\text{no. of equivalent weights} = \frac{\text{weight of substance in g}}{\text{equivalent weight}}$$

$$\text{Normal concentration (N)} = \frac{\dfrac{\text{weight of substance in g}}{\text{equivalent weight}}}{\dfrac{\text{volume of solution in ml}}{1000}}$$

$$= \frac{\text{weight of substance in g} \times 1000}{\text{equivalent weight} \times \text{volume of solution in ml}}$$

$$\text{weight of substance} = N \times \text{equivalent weight} \times \frac{\text{volume ml}}{1000}$$

Example 15

Calculate the number of grams of Na_2SO_4 needed to prepare 200 ml solution of 0.5 N concentration. Equivalent weight of Na_2SO_4 = 71.

$$\text{weight of substance} = N \times \text{equivalent weight} \times \frac{\text{volume ml}}{1000}$$

$$\text{weight of } Na_2SO_4 = 0.5 \times 71 \times \frac{200}{1000} = 7.1 \text{ g}$$

Example 16

Calculate the molar (M) and normal (N) concentrations for a solution prepared by dissolving 10.6 g from sodium carbonate Na_2CO_3 in a liter of the solution. Molecular weight of Na_2CO_3 = 106.

$$\text{no. of moles of } Na_2SO_4 = \frac{\text{weight}}{\text{molecular weight}}$$

$$= \frac{10.6}{106} = 0.1$$

$$\text{Molarity (M)} = \frac{\text{no. of moles of solute}}{\text{volume of solution in liter}} = \frac{0.1}{1} = 0.1$$

$$\text{no. of equivalent weights of } Na_2SO_4 = \frac{\text{weight}}{\text{equivalent weight}} = \frac{10.6}{106/2}$$

$$= 0.2$$

$$\text{Normality (N)} = \frac{\text{no. of equivalent weights}}{\quad} = \frac{0.2}{\quad} = 0.2$$

volume of solution in liter   1

**** Relationship between Molarity (M) and Normality (N)***

N = M × no. of equivalents

Example 17

Calculate the molar (M) concentration of H_3PO_4 solution of 0.250 N, to produce phosphate ion PO_4^{3-}.

N = M × no. of equivalents

0.25 = M × 3

M = 0.0833 Molar

7- *Molal concentration (m)*

It is the number of molar masses (moles) of the dissolved substance in 1000 g of the solvent, whatever is the total volume of the solution.

$$\text{Molal concentration (m)} = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{weight of solvent in g}}$$

Example 18

Calculate the molal (m) concentration m for ethanol in a solution prepared by dissolving 92.2 g ethanol in 500 g water. Molecular weight for ethanol = 46.1.

$$\text{Molal concentration (m)} = \frac{\text{weight of substance in g} \times 1000}{\text{molecular weight} \times \text{weight of solvent in g}}$$

$$= \frac{92.9 \times 1000}{} = 4\ \text{m}$$

$$46.1 \times 500$$

**** The mole fraction***

The mole fraction for solvent is the number of moles of solvent relative to the total number of moles, and the mole fraction for solute is the number of moles of solute relative to the total number of moles. If we multiply the mole fraction by 100 the product is mole percent.

Example 19

Calculate the mole fraction for ethanol C_2H_5OH and water in a solution prepared by dissolving 13.80 g of ethanol in 27 g water. Atomic weight for O=16, C=12, H=1.

$$\text{no. of moles of ethanol} = \frac{\text{weight}}{\text{molecular weight}} = \frac{13.80}{46} = 0.30 \text{ mole}$$

$$\text{no. of moles of water} = \frac{\text{weight}}{\text{molecular weight}} = \frac{27}{18} = 1.50 \text{ mole}$$

the total number of moles = 0.30 + 1.50 = 1.80 mole

$$\text{mole fraction for ethanol} = \frac{\text{moles of ethanol}}{\text{total no. of moles}} = \frac{0.30}{1.80} = 0.167$$

$$\text{mole fraction for water} = \frac{\text{moles of water}}{\text{total no. of moles}} = \frac{1.50}{1.80} = 0.833$$

The highest value for mole fraction is 1, so it is possible to calculate mole fraction for water by determining mole fraction for ethanol:

mole fraction for water = 1 – mole fraction for ethanol

= 1- 0.167 = 0.833

**** Solutions Normality***

The concentration of an acid can be calculated as follow: $N = \dfrac{D \times \% \times 1000}{\text{equivalent weight} \times 100}$

D = density.

To dilute a solution:

$$\underset{\text{before dilution}}{N_1 \times V_1} = \underset{\text{after dilution}}{N_2 \times V_2}$$

**** Concentration Conversions***

**** ppt, ppm, and ppb***

ppb = ppm × 1000

ppb = ppt × 10^6

ppm = ppt × 1000

**** ppm and M***

Convert 78 ppm of Ca^{2+} ions to mol/L.

$$\text{ppm} = \frac{\text{mg solute}}{\text{kg solvent}}$$

78 ppm = 78 mg Ca^{2+} / L of solution = 0.078 g/L

Divide by the atomic weight for calcium ion:

0.078 g/L divided by 40.08 g/mol = 0.0019 mol

ppt = M × M wt.

ppm = M × M wt. × 1000

ppb = M × M wt. × 1000,000

**** ppm and %***

Convert 0.0002% to ppm

$$\frac{0.0002}{100} = \frac{X\ gm}{1000000}$$

X= 2 ppm

% = ppt/10

% = ppm/10,000

% = ppb/10,000,000

****M and %***

Calculate the molarity of 9% NaCl solution. Na= 23, Cl=35.5

$$9 = \frac{9\ gm}{100\ ml} = \frac{9\ gm \times 10}{100\ ml \times 10} = 90 = \frac{90\ gm}{1\ L}\ g/L$$

$$M = \frac{\text{no. of moles}}{1\ L} = \frac{\text{Wt. in g / M.wt}}{1} = \frac{90}{58.5} = 1.538$$

M = % × 10 / M wt.

N = % × 10 / Eq wt.